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(54) **A method for permanently marking x-ray screens**

(57) A method for permanently marking X-ray screens is provided wherein an area of the surface of the screen is brought in contact with a dyestuff and wherein the screen is heated. The application of the dyestuff proceeds preferably image-wise by applying a solvent based ink by an ink-jet printer.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a method for permanently marking objects having a hard polymeric surface. It relates especially to a method for marking X-ray screens, direct emitting screens as well as storage phosphor screens.

BACKGROUND OF THE INVENTION

[0002] In the art of marking objects having a hard polymeric surface it is not self-evident to have a fast, reliable method for producing a mark that is not easily removed by organic solvents, e.g. alcohols, acetone, hexane, etc. or by physical wear.

[0003] In the art of making X-ray screens, it is advantageous to provide such a screen with a protective layer on the phosphor layer. This is the case for X-ray screens comprising direct emitting phosphors as well as for X-ray screens comprising photostimulable or storage phosphors. The protective layer protects the phosphor in the phosphor layer from environmental influences, e.g., humidity, vapours etc. and protects the screen against physical damage during use. The protective layer is frequently a hard polymeric layer, making the screen almost insensitive to scratches during use and other forms of physical damage. Such a protective layer can be produced by applying a polymeric composition on top of the phosphor layer and chemically hardening it, as disclosed in **EP-A- 514 146** or in **US-A-4 205 116.** In many cases a radiation cured protective layer, as disclosed in **EP-A-510 754** is applied to the phosphor layer.

[0004] In radiographic departments using the screens, it is also common usage to clean such screens with organic solvents to remove dust, fingerprints, etc. The cleaning solution comprises frequently methylethylketone and ethanol as solvent.

[0005] On the other hand the producer of the screen wants the screen to be marked so that for each screen the manufacturing history can easily be traced. The radiologist wants that the mark of the screen is printed on the film when a radiograph is made with a light sensitive film in contact with the screen, so as to be able to trace at any moment the film/screen pair used to form the radiological image. Furthermore, it is an advantage that the mark on the screen is easily readable in a dark room, so that when cassettes are manually loaded, it can be checked which screen is present in the cassette at hand. Also official control organisms are demanding a durable marking on X-ray screens. The marking on an X-ray screen is not only required for traceability purposes, but in certain radiographic procedures, e.g., in orthopaedics, the X-ray screens that are used comprise marks, e.g. a grid, that make it possible to measure skeletal distances in the radiographs.

[0006] The typical lifetime of an X-ray screen in an hospital is usually not less than five years, thus any marking on the screen must be very durable and must withstand repeated cleaning. The producer of the screen further demands that the marking of the screen can proceed in such a way that the production process has not to be disturbed by the marking of the screens. It is clear, from the above, that he demands on a mark on an X-ray screen are quite severe both in terms of visibility and in terms of durability.

[0007] It is therefore still desirable to provide a further method for permanently marking X-rays-screens.

OBJECTS AND SUMMARY OF THE INVENTION

[0008] It is an object of the invention to provide a method for permanently marking X-ray screens.

[0009] It is a further object of the invention to provide a method for marking a X-ray screens with a marking that can withstand repeated rubbing with organic solvents.

[0010] It is an other object to provide a simple and cost effective method for marking X-ray screens with a marking that can withstand repeated cleaning and that is visible on the diagnostic images made by using the screen.

[0011] It is a further object of the invention to provide a method for marking an X-ray screen with a mark that withstands physical stresses during the use of the screen and wherein the marking does not deteriorate the physical strength of the X-ray screen.

[0012] Further objects and advantages will become clear from the description hereinafter.

[0013] The objects of this invention are realised by providing a method for marking a X-ray screen having phosphor layer and a protective layer on top of it, forming a first surface of said screen, comprising the steps of :

- contacting an area of said first surface of said X-ray screen with a dyestuff, and
- heating said screen.

[0014] In a preferred embodiment of the invention, said dyestuff is image-wise applied on an area of said first surface of said screen, forming an image having dyed and non-dyed areas and both said dyed and non-dyed areas of said image or only said dyed areas are heated.

[0015] The objects of this invention are further realised in still another specific embodiment of this invention by providing a method for marking a X-ray screen having a protective layer forming a first face of said screen, comprising the steps of :

- covering an area of said first surface of said screen with a dyestuff,
- image-wise heating said area covered with said dyestuff, and

- removing the non-heated dyestuff from said surface, thus forming an image.

DEFINITIONS

[0016] The wording "X-ray" has to be understood as all penetrating radiation and includes i.a. radiation originating from a radioisotope (e.g. a Co60 source), radiation created by an X-ray generator of any type, radiation and high energy particles created by a high energy radiation generator (e.g. Betatron), radiation from a sample labelled with a radioisotope as is the case in e.g. autoradiography.

[0017] The wording "X-ray screen" is used to indicate an intensifying screen, i.e. a supported or self-supporting panel comprising a direct emitting phosphor as well as to indicate a storage screen or photostimulable screen, i.e. a supported or self-supporting panel comprising a storage phosphor or a photostimulable phosphor.

[0018] The word "phosphor" is used to indicate a direct emitting phosphor as well as to indicate a storage or photostimulable phosphor.

[0019] The word "dyestuff" is used to indicate a water or organic solvent soluble dye as well as a pigment.

[0020] The word "mark" and the word "image" are in the context of this invention to be understood as a symbol, alphanumeric characters, a picture, a bar code, a combination of the foregoing, etc. In short these words are meant to indicate any permanent means on the X-ray screen that makes it possible to identify a particular screen.

DETAILED DESCRIPTION OF THE INVENTION

[0021] An X-ray screen can be either self supporting or can comprise a mixture of a phosphor and a binder, coated on a support.

[0022] Typical binders are, e.g., gelatine, polysaccharides such as dextran, gum arabic, and synthetic polymers such as polyvinyl butyral, polyvinyl acetate, nitrocellulose, ethylcellulose, vinylidene chloride-vinyl chloride copolymer, polyalkyl (meth)acrylate, vinyl chloride-vinyl acetate copolymer, polyurethane, cellulose acetate, cellulose acetate butyrate, polyvinyl alcohol, polystyrene, polyester, etc. These and other useful binders are disclosed e.g. in **US-A- 2 502 529, US-A- 2 887 379, US-A-3 617 285, US-A- 3 300 310, US-A- 3 300 311** and **US-A- 3 743 833**. A mixture of two or more of these binders may be used, e.g., a mixture of polyethyl acrylate and cellulose acetobutyrate. Other useful binders in X-ray screens are hydrogenated styrene-diene block copolymers, having a saturated rubber block, as rubbery and/or elastomeric polymers. The polymer can be represented by the formula A-B-A (tri-block) or by the formula A-B (di-block), wherein A represents styrene and B represents the hydrogenated diene block e.g. ethylene-butylene or ethylene-propylene. Such binders have been disclosed in, e.g., **EP-A- 647 258** and **EP-A- 648 254**. Also binders with Tg ≤ 0 °C and being soluble for at least 5 % wt/wt in ethylacetate can beneficially be used in X-ray screens, as disclosed in **EP-A- 758 012**.

[0023] The weight ratio of phosphor to binder is generally within the range of from 50:50 to 99:1, preferably from 80:20 to 99:1, the ratio by volume of phosphor to binding medium is usually more than 70/30 and even more than 85/15. The coating weight of the phosphor particles can be adapted to the desired speed of the radiographic screen or panel, but preferably a coating weight between 5 and 250 mg/cm^2, most preferably between 20 and 175 mg/cm^2, is used.

[0024] On top of the phosphor layer a protective layer is generally applied. This protective layer is mostly in direct contact with the phosphor layer, but this is not necessarily so, thin auxiliary layers (conductive layers, layers containing filter dyes, etc.) can be present between the phosphor layer and the protective layer. Typical protective layers comprise nitrocellulose, ethylcellulose, cellulose acetate or polymethyl(meth)acrylate resin, coated from a solvent. A protective layer on top of the phosphor layer is very often made by coating a radiation (Ultra Violet radiation or electron beam radiation) curable solution on top of the phosphor layer and by curing this solution. The protective layer that is formed in this way not only protects the phosphor containing layer from mechanical and chemical damage but can be given a relief structure for high ease of manipulation, thereby avoiding sticking, friction and electrostatic attraction while keeping of an excellent image resolution. Radiation cured protective layers have been disclosed in, e.g., **EP-A- 510 753** and **EP-A 510 754**.

[0025] It has been found that a permanent mark or image on an X-ray screen having a phosphor layer and a protective layer on top of the phosphor layer could easily be produced from the side of the X-ray screen carrying the protective layer by bringing the surface of the screen carrying the protective layer in contact with a dyestuff and heating the screen and thus also the dyestuff. It was found that such a method provided very good results on X-ray screens having a radiation cured protective layer as described above. The mark that was produced had a very high resistance to physical stresses, e.g., repeated loading of a film in a cassette while letting the film edge scrape over the mark did almost not deteriorate the mark. The mark withstood also repeated rubbing with organic solvents. By selecting the dyestuff so has to have a hue different from the hue of the screen surface, the readability of the mark by a human observer can be maximised and by selecting the dyestuff so as to have an high absorbency for the light emitted by a prompt emitting X-ray screen the impression of the mark on the final radiological image produced while using the screen becomes easy. Also when a photostimulable screen is used to record the X-rays, the hue of the dyestuff can be chosen so as to

strongly absorb the light that is emitted upon photostimulation. By doing so the hard-copy film can easily be provided by the mark of the screen that was used.

[0026] The general principle of the invention, bringing a dyestuff in contact with the surface of an X-ray screen and heating the screen, can be practised in various embodiments.

First embodiment

[0027] It was found that thermo-sublimation printing on the surface of the X-ray screen carrying the protective layer, by contacting a dye donor material with the surface of the X-ray screen and image-wise heating said donor material could produce a permanent mark or image on the screen. Thus, using classical donor materials (e.g. the donor material that is used in a DRYSTAR, - trade name of Agfa-Gevaert NV, Mortsel, Belgium - printer) and a thermal printhead wherein the heating was image-wise modulated, a permanent mark with an acceptable density could be produced on an X-ray screen. The thermo-sublimation printing described immediately above, is a first embodiment of the general method of this invention : contacting an area of the surface of the X-ray screen with a dyestuff and heating the surface. In this first embodiment, the dyestuff is non-image wise contacted with an area of the surface of the screen and then the dyestuff is heated in accordance with image data. The first embodiment of the present invention can also be accomplished by contacting an area of the surface of the screen to an hot-stamping-foil and then hot-stamping the desired information on the screen. This again is a method wherein the dyestuff is non-image wise contacted with an area of the surface of the screen and then the dyestuff is heated in accordance with image data. It may be beneficial to treat the area of the surface of the screen that is to be contacted by the hot-stamping-foil first with a corona discharge, producing a very stable mark on the screen.

Second embodiment

[0028] In the second embodiment of the invention, the dyestuff is image-wise applied to an area of the surface of the screen and then that area (or if so desired, the whole the screen) is heated. Although aqueous dispersions of pigments can be used to bring the dyestuff on the surface of the screen, it is preferred, in the method according to this invention, to apply the dyestuff from a solution of one or more dyes in an organic solvent to the surface of the X-ray screen, i.e. solvent based inks are preferably used. Solvent based inks are, for the method according to this invention, also inks that comprise as solvent less than 50 % by volume of water, the remainder being an organic solvent compatible with water, e.g., lower alcohols (methanol, ethanol, n-propanol and isopropanol), ketones (acetone and methylethylketone), glycols (ethylene glycol, triethyleneglycol), dioxane, etc. Typical solvent based inks, that can be used in the method according to the present invention have been disclosed in ,e.g., **DE-A- 31 35 800, WO-A- 97 17409, EP-A-764 700** and **US-A-5 160 535.**

[0029] The solution of at least one dye in an organic solvent is preferably applied by ink-jet printing and said solution is preferably a solvent based ink.

[0030] The dyestuff can also be applied to an area of the screen to be marked by electrostatographic methods, using dyed or pigmented toner particles as marking material. The toner particles can be applied by lquid development as well as by dry development. The latter development is preferred when the dyestuff is applied to the screen by lectrostatographic methods. The dry toner particles are, although any electrostatic method known in the art can be used, preferably applied by a method of direct electrostatic printing wherein toner particles are image-wise projeted from a toner source on the screen and wherein no electrostatic latent image intervenes. Methods for direct electrostatic printing useful in this invention are methods as described in, e.g., **EP-A-740 224, EP-A-675 417, EP-A-435 549**, etc..After deposition of the toner particles, the toner particles are fixed to the screen by heating.

[0031] The heating of the dye can proceed by contacting the surface of the screen with an heated body, by contacting the rear surface (i.e. the surface of the screen opposite to the surface whereon a phosphor layer and a protective layer are present) of the X-ray screen with an heated body, the heating can proceed by Infra Red Radiation Lamps, by a laser emitting light in a wavelength range between 480 and 1200 nm, preferably emitting light in a wavelength range between 700 and 1200 nm, e.g., a Nd:YAG laser, a diode laser or a semiconductor laser. A typical useful semi-conductor laser is a GaAs-laser emitting around 830 nm, e.g., the GaAs laser sold by Laser Diode Labs, 80 Rose Orchard Way, San Jose, CA, USA under trade name SDL-8110. Also a CO_2-laser emitting at 10,640 nm is useful in this invention.

[0032] Preferably the heating proceeds in non-contact mode by infra red radiation of an infra red lamp or infra red emitting laser. Since the heating proceeds preferably by radiation, it is preferred to use ink-jet inks comprising infra-red absorbing substances or, in the simplest form, black inks. A typical useful black ink is the ink sold by the STEADTLER J. S. & Co, of Germany under trade name 48304-9NEU LP29017. This embodiment of the invention secures high density printing using ink-jet printing which is a proven method for image-wise applying dyestuffs on a surface. The possibility of overall heating of the screen or the area having received the mark simplifies the apparatus : the marking with the method according to this invention can proceed on-line, when at the end of the production line of the screen an ink-jet printer is installed followed by an infra red emitter.

Third embodiment

[0033] In the third embodiment of the method of this invention, the dyestuff is image-wise applied to an area of the surface of the screen as described in the second embodiment of the invention and then only the image is heated. Thus in this embodiment both the application of the dyestuff and the heating proceed image-wise and the image data for addressing the ink-jet printer are also used for addressing the heat source. The image-wise application of the dyestuffs can be carried out by the ways and means described above for the second embodiment of the invention.

[0034] Although lasers emitting in a wavelength range from 480 to 1200 nm can be used, depending on the light absorption characteristics of the dyestuff that is used, to image-wise heating the image-wise applied dyestuff, the preferred heat source for image-wise heating in this embodiment is an infra red emitting laser, i.e. a laser emitting in a wavelength range from 700 to 1200 nm. It is preferred to use an infra red emitting diode or semiconductor laser. A very useful diode laser for use in the second embodiment of the invention is a GaAs diode laser sold by Spectra Diode Labs, 80 Rose Orchard Way, San Jose, CA, USA, under trade name SDL-8110. The advantage of this third embodiment lays in the very local heating of the X-ray screen so that possible damage of the screen due to (excessive) heating is avoided. Moreover the ink-jet printhead and the diode laser can be built so as to move together so that the written image is heated immediately.

Fourth embodiment

[0035] In a fourth embodiment of the invention, the dyestuff is non-image-wise applied to an area of the surface of the X-ray screen, then the area covered with the dyestuff is image-wise heated and the dyestuff that not has been heated is removed, thus leaving an image on the X-ray screen. The dyestuff can non-image-wise be applied from aqueous dispersions of pigments on said area of the surface of the screen. It is preferred, in the fourth method according to this invention, to apply the dyestuff from a solution of one or more dyes in an solution comprising an organic solvent to the surface of the screen, i.e. with solvent based inks or paint, such as described above under the second embodiment of the invention.

[0036] The non-image-wise application of the dispersion or solution containing a dyestuff on an area of the surface of the X-ray screen can proceed by any means known in the art, e.g., spraying, coating, application by a wick soaked in the solution, etc.

[0037] The image-wise heating can proceed while the area, whereon the dyestuff is applied, is still wet. In that case it is preferred to use non-contact heating by infra red radiation of an infra red lamp, an infra red emitting laser, an infra red emitting diode or infra red emitting semiconductor laser A very useful diode laser for use in the fourth embodiment of the invention is a GaAs sold by Spectra Diode Labs, 80 Rose Orchard Way, San Jose, CA, USA under trade name SDL-8110..

[0038] The area, whereon the dyestuff is applied can also be dried before the image-wise heating. It is then still preferred to use non-contact heating for the image-wise heating, but it is possible, with good results, to use a thermal printhead to perform the image-wise heating as in the first embodiment of this invention.

[0039] The non-heated dyestuff can be removed by simply brushing the remaining dyestuff away, by wiping it away with a solvent, an organic solvent or water, depending on the nature of the solvent used when applying the dyestuff to the surface of the X-ray screen. The wiping can proceed by rubbing a cloth soaked in the solvent over the dyed area of the screen, rinsing the screen with the solvent, brushing the solvent over the screen, dissolving the remaining dye, etc..

Claims

1. A method for marking a X-ray screen having phosphor layer and a protective layer on top of it, forming a first surface of said screen, comprising the steps of :
   - bringing an area of said first surface of said X-ray screen in contact with a dyestuff, and
   - heating said screen.
2. A method according to claim 1, wherein only said area in contact with a dyestuff is heated.
3. A method according to claim 1, wherein said area in contact with a dyestuff is image-wise heated.
4. A method according to any of claims 1 to 3, wherein said area of said first surface of said X-ray screen is brought in contact with a dyestuff by image-wise applying said dyestuff on said area of said first surface of said screen, forming an image having dyed and non-dyed areas.
5. A method according to claim 4, wherein said dyestuff is applied to said area by ink-jet printing.
6. A method according to claim 5, wherein said ink-jet printing proceeds with a solvent based ink.
7. A method for marking a X-ray screen having phosphor layer and a protective layer on top of it, forming a first surface of said screen, comprising the steps of :
   - covering an area of said first surface of said screen with a dyestuff,
   - image-wise heating said area covered with

said dyestuff, and

- removing the non-heated dyestuff from said surface forming an image on said surface.

8. A method according to any one of the preceding claims, wherein said heating proceeds by non-contact heating means.

9. A method according to claim 8, wherein said non-contact heating means is an infra red emitting device.

10. A method according to claim 9, wherein said infra-red emitting device is an infra red emitting diode laser.

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EUROPEAN SEARCH REPORT

Application Number
EP 97 20 3176

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DATABASE WPI Section Ch, Week 8729 Derwent Publications Ltd., London, GB; Class K08, AN 87-202386 XP002059312 & JP 62 130 400 A (FUJI PHOTO FILM CO LTD) , 12 June 1987 * abstract *		G21K4/00 G03C11/02 G03C5/17
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 April 1998	Philosoph, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 97 20 3176

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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